S.F.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: **Pirimiphos-methyl** (List B, Case No. 2535/Chemical ID No. 108102). Guideline Nos. 860.1500/1520/1480. Magnitude of the Residue in Stored Grain and Processed Fractions; Storage Stability Data.

MRID Nos. 44039501, 44073901; 44073902; 44097801; 44129601; 44155701.
DP Barcode Nos. D227552; D228760; D229663; D230598; and D231449.
CBRS Nos. 17423; 17495; 17581; 17619; and 17666.

FROM: Christina B. Swartz, Chemist
Reregistration Branch I
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THROUGH: Whang Phang, Ph.D., Branch Senior Scientist 10/16/97
Reregistration Branch I
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TO: Frank Rubis/Arnold Layne (PM 51)
Accelerated Reregistration Branch
Special Review and Reregistration Division (7508W)

HED has completed its review of residue studies submitted by Wilbur Ellis Co. in support of continued registration of the active ingredient pirimphos-methyl for use on stored grain. The review was completed by Dynamac under supervision of HED, and has been revised to reflect current Agency policy.

The studies depicting the magnitude of pirimiphos-methyl residues in stored grain and processed commodities are adequate to support the registered use and tolerance reassessment, pending submission of acceptable storage stability data.

A new storage stability study should be initiated. Grain (sorghum or corn), corn oil and aspirated grain fractions samples should be fortified with pirimiphos-methyl and R36341, stored frozen, and analyzed after intervals representative of the storage intervals incurred in the corn, sorghum and wheat residue studies.

Tolerance reassessment will be conducted in conjunction with the preparation of a residue chemistry chapter of the HED reregistration eligibility document (RED) chapter. The submitted data indicate that tolerances for residues in sorghum and corn grain should be increased to 20 ppm, leading to the need for an increased tolerance for residues in corn oil to 160 ppm, and the need for a tolerance for residues in aspirated grain fractions at 50 ppm. Tolerances for residues in sorghum and corn milled fractions should be revoked [residues did not concentrate in corn milled fractions, and EPA no longer sets tolerances for residues in sorghum milled fractions]. If a tolerance is established for pirimiphos-methyl residues in wheat grain, a separate tolerance for residues in wheat flour will not be required.

HED notes that the reassessment of grain tolerances at higher levels may result in unacceptable dietary risks; if acceptable storage stability data demonstrate significant declines in residue levels during the storage intervals incurred in the submitted studies, then tolerances may need to be reassessed even higher. The submitted residue data could support lower tolerances, if fewer applications are specified. An immunoassay method for determining residues in stored grain has been validated by the Agency. SRRD may want to consider consulting with OGC to determine the feasibility of various approaches for risk managment.

cc: CSwartz; List B Rereg. File; SF; RF;
CSwartz:RRB1:CM2:Rm804F:703 305 5877:10/3/97
RDI:WJH:10/9/97 RRB1ExpoTeam:10/8/97

PIRIMIPHOS-METHYL

Shaughnessy No. 108102; Case 2535

(CBRS Nos. 17423, 17495, 17581, 17619, 17666; DP Barcodes D227552, D228760, D229663, D230598, D231449)

Registrant's Response to Residue Chemistry Data Requirements

March 25, 1997

Contract No. 68-D4-0010

Submitted to:
U.S. Environmental Protection Agency
Arlington, VA

Submitted by:
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PIRIMIPHOS-METHYL

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REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY DATA REQUIREMENTS

BACKGROUND

The Pirimiphos-methyl Phase IV Review (1/91) required magnitude of the residue and processing studies on corn, sorghum, and wheat. Grain was to be treated prior to storage and samples analyzed for pirimiphos-methyl and regulated metabolites. Storage stability data were required to support all residue studies. In response, Compliance Services International, on behalf of the Wilbur-Ellis Company, has submitted the following data: magnitude of the residue on corn and sorghum with storage stability data (1996; MRIDs 44073901 and -02); processing studies on corn, sorghum, and wheat (1996; MRIDs 44155701, 44097801, and 44129601); and additional storage stability data (1993; MRID 44039501). These data are reviewed in this report for their adequacy in fulfilling outstanding residue chemistry data requirements.

Tolerances are established (40 CFR §180.409) for residues of pirimiphos-methyl and its metabolite O-[2-ethylamino-6-methyl-pyrimidin-4-yl) O,O-dimethyl phosphorothioate and, in free and conjugated form, the metabolites 2-diethylamino-6-methyl-pyrimidin-4-ol, 2-ethylamino-6-methyl-pyrimidin-4-ol, and 2-amino-6-methyl-pyrimidin-4-ol in corn (8.0 ppm), sorghum grain (8.0 ppm), kiwifruit (5.0 ppm), eggs (0.5 ppm), milk fat (3.0 ppm; 0.1 (N) in whole milk); fat of cattle, goats, hogs, horses, poultry, and sheep at 0.2 ppm; kidney and liver of cattle, goats, hogs, horses, and sheep at 2.0 ppm; meat and meat byproducts of cattle, goats, hogs, horses, and sheep at 0.2 ppm; and meat and meat byproducts of poultry at 2.0 ppm. Food and feed additive tolerances have been established in 40 CFR §185.4950 and 186.4950 for residues in corn milling fractions (except flour) and sorghum milling fractions (except flour) at 40 ppm and in 40 CFR §185.4950 for residues in corn oil at 88 ppm. The tolerances for residues in corn and sorghum grain were established for postharvest application to stored grain.

CONCLUSIONS AND RECOMMENDATIONS

1. The **corn grain** residue data are adequate. In seven trials, stored grain received five 1X applications at 60- to 90-day intervals over a period of 270 days. Samples were collected 0-90 days after each application. The highest residue of 336 samples was

18.8 ppm and the highest average field trial (HAFT) residue value was 12.7 ppm. The des-ethyl metabolite R36341 was a minor component of the residue at ≤0.08 ppm.

2. The **sorghum grain** residue data are adequate. In seven trials, stored grain received five 1X applications at 60- to 90-day intervals over a period of 270 days. Samples were collected 0-90 days after each application. The highest residue was 18.2 ppm and the HAFT was 17.2 ppm.

3. The corn, sorghum and wheat processing studies are adequate:

   - Residues concentrated at an average of 12.2x in refined corn oil and 3.8x in aspirated grain fractions of corn; residues did not concentrate in other milled fractions.

   - Residues concentrated in aspirated grain fractions of sorghum at 2.3x. Residues did not concentrate in sorghum flour.

   - Combined residues in wheat grain were 29.5 ppm. Residues concentrated by a factor of 2.1x in wheat bran and by a factor of 3.4x in aspirated grain fractions of wheat. Residues did not concentrate in wheat flour.

4. All grain and processed commodity samples were analyzed using Method CSI-011, a gas chromatographic method employing flame photometric detection (GC/FPD) for determining pirimiphos-methyl and its des-ethyl metabolite (R36341); the method is adequate for data collection. Recoveries of pirimiphos-methyl and R36341 from fortified samples were adequate in validation tests and analyses of fortified samples analyzed concurrent with residue samples. The method is listed in PAM, Vol. II as Method I, and is specified for kiwifruit.

5. The available storage stability data are not adequate to support residue trials in stored grain. One study revealed residue decline in corn and sorghum grain stored frozen for 4 months, but was not continued over longer intervals. Samples from the residue trials on corn and sorghum grain were stored for up to 32 months. In another study a 45% residue decline was observed in corn grain, with an 8% decline in residues in sorghum grain, and a 47% residue increase in wheat grain between two analyses conducted 4 years apart. Although there have been apparent declines in pirimiphos-methyl and R36341 residues in frozen grain during storage, HED cannot use the available data to determine an appropriate decline factor. A new storage stability study is required.

6. Tolerances for pirimiphos-methyl residues will be reassessed in conjunction with the preparation of the residue chemistry chapter of the HED reregistration eligibility decision document (RED) chapter and concomitant risk assessment. The submitted data indicate the following tolerance reassessments will be needed:

- Tolerances for residues in sorghum and corn grain should be increased to 20 ppm, which leads to an increase in the corn oil tolerance to 160 ppm, and the need for a tolerance for residues in aspirated grain fractions at 50 ppm.
- Tolerances for residues in sorghum and corn milled fractions should be revoked. If a tolerance is established for pirimiphos-methyl residues in wheat grain, a separate tolerance for residues in wheat flour will not be required.

7. HED notes that the reassessment of grain tolerances at higher levels may result in calculation of unacceptable dietary risks; if acceptable storage stability data demonstrate significant declines in residue levels during the storage intervals incurred in the submitted studies, then tolerances may need to be reassessed even higher. The submitted residue data could support lower tolerances, if fewer applications are specified. An immunoassay method for determining residues in stored grain has been validated by the Agency. SRRD may want to consider consulting with OGC to determine the feasibility of various approaches for risk managment.

DETAILED CONSIDERATIONS

Magnitude of the Residue in Stored Grain

Corn grain (MRID No. 44073902)

Seven trials were conducted in CA, GA, IN, KS, ND, PA, and TX, in which corn grain was treated 5 times on study days 0, 90, 150, 210, and 270 (±5 days) at a target rate of 0.48 lb ai/30 tons of stored grain (1x, 5 lb/gal EC formulation). Spray treatments were made as grain was augured from a holding bin into the storage bin. Actual application rates ranged from 0.38-0.58 lb ai/30 tons of corn grain. The totals for the five applications for each location were 2.32-2.71 lb ai/30 tons for averages of 0.46-0.54 lb ai/30 tons/application. At each test site, three replicate treated samples were taken on days 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, and 330 (±6 days). Control samples were collected on these same days prior to collection of treated samples. On treatment days, sampling was conducted before and after treatment. Samples were frozen at the test sites, shipped frozen to CSI, and stored frozen for 1-28 months prior to analysis.

Sorghum grain (MRID No. 44073901)

Seven trials were conducted in CA, GA, IN, KS, ND, PA, and TX, in which grain was treated 5 times on study days 0, 90, 150, 210, and 270 (±5 days) at a target rate of 0.48 lb ai/30 tons of stored grain (1x, 5 lb ai/gal EC formulation). Spray treatments were made as grain was augured from a holding bin into the storage bin. Actual application rates ranged from 0.43-0.59 lb ai/30 tons of sorghum grain. The totals for the five applications for each location were 2.36-2.50 lb ai/30 tons for averages of 0.47-0.50 lb ai/30 tons/application.

Three replicate treated samples were taken on days 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, and 330 ($\pm$10 days). Control samples were collected on these same days prior to collection of treated samples. On treatment days, sampling was conducted before and after treatment. Samples were frozen at the test sites, shipped frozen to CSI, and stored frozen for 1-32 months prior to analysis.

Magnitude of the Residue in Processed Food/Feed

Corn grain processing (MRID No. 44155701)

Corn grain used for processing was obtained from the trial conducted in TX, in which grain received five applications of pirimiphos-methyl at 54- to 88-day intervals at a target rate of 0.48 lb ai/30 tons of grain (1x). The grain sample was taken on study day 300 approximately 30 days after the fifth application. The sample was stored for 7 days at ambient temperature prior to shipment to Texas A&M University Food Protein Research and Development Center for processing. The grain was stored frozen for approximately 5 months before processing by wet and dry milling procedures similar to commercial practices. Material balances were adequate. Generation of aspirated grain fractions was accomplished prior to the dry milling procedure using a simulation of industrial practice for removal of aspirated grain fractions before terminal elevator storage. Samples of whole grain were stored for 16 months prior to analysis and processed fractions were stored up to 18 months.

Sorghum grain processing (MRID No. 44097801).

Sorghum grain used for processing was obtained from a trial conducted in TX, in which grain received five applications of pirimiphos-methyl at 54- to 87-day intervals at a target rate of 0.48 lb ai/30 tons of grain (1x). The grain sample was taken on study day 302 approximately 30 days after the fifth application. The sample was stored for 7 days at ambient temperature prior to shipment to Texas A&M University Food Protein Research and Development Center for processing. The grain was stored frozen for approximately 5 months before processing into flour and aspirated grain fractions. Material balances were adequate. Prior to analysis samples of whole grain were stored frozen for 21 months and processed fractions were stored frozen for 16 months.

Wheat grain processing (MRID No. 44129601)

In a trial conducted in MT, wheat grain received five applications of pirimiphos-methyl at 55- to 93-day intervals at a target rate of 0.48 lb ai/30 tons of grain (1x). Actual application rates were 0.47-0.53 lb ai/30 tons. The grain sample was taken on study day 334, approximately 30 days after the fifth application. The sample was stored for 3 days at ambient temperature prior to receipt by Wm. Englar & Associates (Moses Lake, WA) for processing into flour and milled fractions and at Texas A&M University Food Protein Research and Development Center for processing into aspirated grain fractions. Processing procedures simulated commercial practice. Material balances were adequate. The grain was stored frozen for approximately 2-4 months before processing, and for 4 months prior to analysis. Milled fractions were stored for 2 months between processing and analysis. Aspirated grain fractions were stored for 2.5 years prior to analysis.

Residue Analytical Methods

Residues of pirimiphos-methyl and des-ethyl pirimiphos-methyl (R36341) in corn, sorghum, and wheat and grain processed fractions were determined using Method No. CSI-011 (versions -04 and -06), "Analytical Method for the Determination of Pirimiphos-methyl and Des-ethyl Pirimiphos-methyl in Wheat, Corn, Sorghum, and Grain Fractions by Gas Chromatography," developed by Compliance Services International. The methods are modifications of Method I in PAM, Vol. II.

Briefly, residues in grain, aspirated grain fractions and non-oily processed fractions are extracted with toluene and partitioned against water. The toluene extract is dried over sodium sulfate and concentrated by evaporating under vacuum. Residues are analyzed using gas chromatography with flame photometric detection in the phosphorus mode (GC/FPD). The method for corn oil utilizes acetonitrile (ACN) as the extracting solvent. Oil is separated from the ACN extract by chilling and the ACN extract is evaporated to near dryness. The residue is exchanged from ACN to toluene by addition of a small amount of toluene as the extract nears dryness. Residues in the final extract are analyzed using GC/FPD.

In corn and sorghum commodities, limits of quantitation (LOQs) for pirimiphos-methyl and des-ethyl pirimiphos-methyl (R36341), respectively were: 0.05 and 0.05 ppm in grain, grits, starch, flour, and meal; 0.25 and 0.05 ppm in corn oil; and 0.25 and 0.20 ppm in aspirated grain fractions. In wheat grain and milled fractions the LOQ was 0.1 ppm for both parent and the des-ethyl metabolite. Method validation recovery data are summarized in Table 1. Concurrent recovery data submitted with magnitude of residue studies are summarized in Table 2. Validation and analyses of concurrent fortifications demonstrated adequate recoveries; none of the control samples analyzed contained detectable pirimiphos-methyl or R36341 residues. Method CSI-011 for determining pirimiphos-methyl and its des-ethyl metabolite (R36341) is adequate for data collection.

Table 1. Method Validation Data for Pirimiphos-Methyl and R36341 in Grain and Processed Commodities.

Commodity MRID	Pirimiphos-methyl		R36341	
	Fortification (ppm)	Recovery (%)	Fortification (ppm)	Recovery (%)
Corn grain 44155701	0.05-25	83.9-117.1 n=18	0.05-0.5	75.5-119.6 n=18
Corn grits 44155701	0.05-25	90.6-98.5 n=9	0.05-0.5	73.8-108.1 n=9
Corn meal 44155701	0.05-25	85.1-107.2 n=9	0.05-0.5	74.6-104.3 n=9
Corn flour 44155701	0.25-25	92.6-112.2 n=9	0.05-0.5	85.1-113.3 n=9
Corn starch 44155701	0.05-25	87.6-99.2 n=9	0.05-0.5	75.8-103.3 n=9
Corn refined oil (dry milled) 44155701	0.25-25	80.6-94.8 n=9	0.05-0.5	88.3-100.1 n=9
Corn refined oil (wet milled) 44155701	0.25-25	88.8-108.1 n=9	0.25-1.0	93.9-102.2 n=9
Corn grain dust 44155701	0.25-25	79.4-113.9 n=9	0.25-1.0	82.7-117.4 n=9
Sorghum grain 44073901	0.05-25	79.8-114.9 n=20	0.05-0.50	70.6-102.9 n=20
Sorghum flour 44097801	0.05-25	91.0-104.5 n=9	0.05-0.5	75.2-108.6 n=9
Sorghum grain dust 44097801	0.25-25	93.5-116.1 n=9	0.05-0.5	76.2-94.3 n=12

Table 1. Method Validation Data for Pirimiphos-Methyl and R36341 in Grain and Processed Commodities.

Commodity MRID	Pirimiphos-methyl		R36341	
	Fortification (ppm)	Recovery (%)	Fortification (ppm)	Recovery (%)
Wheat grain 44129601	0.1-25	75.0-107.9 n=10	0.1-2.0	84.9-118.4 n=10
Wheat flour 44129601	0.1-25	85.2-110.2 n=9	0.1-0.5	72.8-115.6 n=9
Wheat bran 44129601	0.1-25	74.4-112.0 n=12	0.1-0.5	71.8-91.0 n=12
Wheat middlings	0.1-25	87.0-121.4 n=9	0.1-0.5	71.8-104.9 n=9
Wheat shorts	1.0-10	78.4-101.9 n=4	0.1-0.5	82.8-106.3 n=4
Wheat grain dust	0.25-25	77.3-111.9 n=9	0.05-0.5	86.9-108.7 n=9

Table 2. Concurrent Recoveries of Pirimiphos-Methyl and R36341 from Grain and Processed Commodities.

Commodity Site	Pirimiphos-methyl		R36341	
	Fortification (ppm)	Recovery (%)	Fortification (ppm)	Recovery (%)
Corn grain	0.05-20	83.0-114.5 n=84	0.05-0.20	76.9-116.3 n=82
Corn grain (RAC)	10.0	91.3	0.20	119.3
Corn grits	0.05	91.6	0.05	93.1
Corn meal	10.0	89.5	0.20	91.5
Corn flour	5.0	109.6	0.20	114.3
Corn starch	0.05	118.1	0.05	100.0
Corn dry refined oil	0.50	84.9	0.05	91.4
Corn wet refined oil	1.0	87.1	0.25	104.6

Table 2. Concurrent Recoveries of Pirimiphos-Methyl and R36341 from Grain and Processed Commodities.

Commodity Site	Pirimiphos-methyl		R36341	
	Fortification (ppm)	Recovery (%)	Fortification (ppm)	Recovery (%)
Corn grain dust	20.0	113.6	0.50	114.2
Sorghum grain	0.05-20	80.2-117.9 n=84	0.05-0.15	67.3-119.8 n=84
Sorghum grain (RAC)	10.0	110.8	0.2	91.5
Sorghum flour	0.05	102.0	0.05	97.4
Sorghum grain dust	20.0	84.1	0.5	115.9
Wheat grain (RAC)	20.0	88.9	0.1	100.9
Wheat flour	1.0	90.0	0.1	102.0
Wheat bran	10.0	77.0	0.1	96.0
Wheat middlings	1.0	91.0	0.1	99.7
Wheat shorts	10.0	90.1	0.1	113.7
Wheat grain dust	10.0	94.1	0.2	101.0

Results

Corn Grain/Processed Commodities

The highest average combined pirimiphos-methyl and R36341 residue in corn grain was 12.67 ppm, the average of the three replicate samples taken after application #4 on day 210 in the ND test; the highest single combined residue value from that test was 18.9 ppm. Residues of R36341 were a minor component of the combined residues. Of the 336 treated samples, all but 21 samples contained <0.05 ppm of R36341. Detectable R36341 residues in 21 samples ranged from 0.05-0.08 ppm.

Residues concentrated in refined corn oil up to 13.4x, with an average of 12.2x, and at 3.8x in grain dust. These factors should be applied to the highest average field trial value to obtain appropriate tolerance levels for corn oil and aspirated grain fractions. Based on the HAFT of 12.67 ppm, the tolerance for residues in corn oil should be increased to 160 ppm and a tolerance of 50 ppm for aspirated grain fractions would be appropriate. Residues did not concentrate in other milled fractions, and therefore the tolerance for residues in milled fractions (except flour) should be revoked.

Sorghum Grain/Processed Commodities

The highest average combined pirimiphos-methyl and R36341 residue in sorghum grain was 17.2 ppm, the average of the three replicate samples taken after application #4 on day 210 in the ND test; the highest single combined residue value from that ND test was 18.2 ppm. Of the 336 treated samples reported, all but 65 samples contained <0.05 ppm of R36341. Detectable R36341 residues in 65 samples ranged from 0.05-0.16 ppm.

Residues concentrated in aspirated grain fractions of sorghum at 2.4x. Residues did not concentrate in flour. The tolerances for residues in sorghum milling fractions (except flour) should be revoked, since flour is the only sorghum grain milling fraction for which residues are currently regulated. A tolerance for residues in aspirated grain fractions should be established based on the 4x concentration factor observed in the corn processing study.

Wheat Processed Commodities

Combined residues in wheat grain were 29.5 ppm. Residues concentrated by a factor of 2.1x in wheat bran and by a factor of 3.4x in wheat aspirated grain fractions. Residues did not concentrate in wheat flour. The submission indicated that field trials for wheat grain have been conducted. If a tolerance is established for residues in wheat grain, a tolerance for residues in wheat flour will not be required.

Results of the stored grain treatment trials and the concomitant processing studies are presented in Tables 3 through 7.

Table 3. Combined Residues (ppm) of Pirimiphos-Methyl and R36341 in Stored Corn Grain.

Sampling occasion	Study day	Combined residues (ppm)						
		CA	GA	IN	KS	ND	PA	TX
1	0	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Application 1								
2	0	3.09	1.64	2.85	1.52	2.44	4.87	2.83
3	30	1.90	1.78	1.91	1.81	2.54	3.91	2.72
4	60	1.33	1.53	2.93	1.88	2.72	4.62	2.24

Table 3. Combined Residues (ppm) of Pirimiphos-Methyl and R36341 in Stored Corn Grain.

Sampling occasion	Study day	Combined residues (ppm)						
		CA	GA	IN	KS	ND	PA	TX
5	90	0.80	1.67	3.42	2.00	2.57	4.59	2.25
Application 2								
6	90	3.49	3.63	5.51	6.41	5.11	6.45	4.39
7	120	1.56	3.90	5.39	5.29	3.85	5.52	4.14
8	150	1.75	3.70	4.79	4.90	4.10	5.15	3.93
Application 3								
9	150	4.26	6.06	6.78	8.24	8.60	7.08	7.05
10	180	3.69	3.82	4.85	6.74	9.00	6.45	5.04
11	210	3.73	3.93	4.55	6.46	7.40	6.89	3.61
Application 4								
12	210	5.12	5.41	6.33	8.94	12.67	7.08	5.74
13	240	4.84	7.19	3.89	7.63	10.82	4.01	4.65
14	270	4.46	5.59	3.85	8.29	10.58	7.46	4.72
Application 5								
15	270	6.29	8.74	6.04	9.55	11.37	8.17	7.52
16	300	6.52	5.85	5.94	8.94	11.93	8.89	5.54
17	330	6.71	6.09	6.93	8.08	12.63	8.72	5.31

Table 4. Pirimiphos-Methyl Residues in Corn Processing Commodities.

Fraction	Pirimiphos-methyl (ppm)	R36341 (ppm)	Combined residues (ppm)	Concentration factor
Corn grain (RAC)	7.07	0.05	7.09	NA
Grits	1.35	<0.05	1.40	<1
Meal	2.66	<0.05	2.71	<1
Flour	2.72	<0.05	2.77	<1

Table 4. Pirimiphos-Methyl Residues in Corn Processing Commodities.

Fraction	Pirimiphos-methyl (ppm)	R36341 (ppm)	Combined residues (ppm)	Concentration factor
Starch	0.10	<0.05	0.15	<1
Refined oil (dry milled)	77.0	0.56	77.6	11x
Refined oil (wet milled)	94.3	0.58	94.9	13.4x
Grain dust	26.4	0.26	26.7	3.8x

Table 5. Combined Residues Pirimiphos-Methyl and R36341 in Stored Sorghum Grain.

Sampling occasion	Nominal study day	Combined residues (ppm)						
		CA	GA	IN	KS	ND	PA	TX
1	0	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Application 1								
2	0	3.27	4.14	4.20	2.83	4.07	6.61	3.16
3	30	3.23	3.79	3.80	3.14	4.42	6.46	3.15
4	60	2.00	3.67	3.43	3.38	3.92	5.97	3.14
5	90	2.31	3.66	3.73	3.41	3.70	6.61	3.86
Application 2								
6	90	5.95	7.18	7.96	7.68	7.99	7.33	6.88
7	120	5.88	6.57	7.93	7.59	8.20	7.25	7.74
8	150	5.73	6.08	7.26	7.25	8.27	7.42	6.22
Application 3								
9	150	8.48	10.2	10.9	11.2	11.9	12.5	9.89
10	180	8.21	7.59	10.1	10.1	12.7	11.4	8.41
11	210	7.01	6.84	9.99	9.26	11.9	10.7	10.7
Application 4								

Table 5. Combined Residues Pirimiphos-Methyl and R36341 in Stored Sorghum Grain.

Sampling occasion	Nominal study day	Combined residues (ppm)						
		CA	GA	IN	KS	ND	PA	TX
12	210	9.44	9.25	14.3	14.3	17.2	13.4	8.91
13	240	9.29	8.53	12.0	11.0	15.3	11.3	9.33
14	270	8.70	7.95	12.8	11.1	11.2	11.5	9.13
Application 5								
15	270	11.8	11.4	15.6	12.3	17.1	13.8	11.8
16	300	12.2	10.2	15.0	11.1	16.5	13.0	13.2
17	330	12.6	9.34	13.5	9.11	15.5	12.8	12.7

Table 6. Pirimiphos-Methyl Residues in Sorghum Processing Commodities.

Fraction	Pirimiphos-methyl (ppm)	R36341 (ppm)	Combined residues (ppm)	Concentration factor
Sorghum grain (RAC)	13.44	<0.05	13.9	NA
Flour	2.01	<0.05	2.1	<1
Grain dust	31.73	0.19	31.94	2.3x

Table 7. Pirimiphos-Methyl Residues in Wheat Processing Commodities.

Fraction	Pirimiphos-methyl (ppm)	R36341 (ppm)	Combined residues (ppm)	Concentration factor
Wheat grain (RAC)	29.2	0.26	29.5	NA
Flour	9.24	<0.1	9.24	<1
Bran	60.5	0.23	60.8	2.1x
Middlings	8.77	<0.1	8.77	<1
Shorts	18.4	0.17	18.6	<1
Grain dust	96.6	2.60	99.4	3.4x

Storage Stability Data

Prior to the initial application, corn and sorghum grain samples to be used in the storage stability study were obtained from the GA and KS locations. The samples were fortified with pirimiphos-methyl at 10 ppm and with R36341 at 1.0 ppm, and were placed in frozen storage for 0-4 months prior to analysis. The results of the storage stability study are summarized in Table 8.

Table 8. Stability of Pirimiphos-Methyl and R36341 Residues in Stored Grain.

Storage interval (months)	Fortification (ppm)	Corrected recovery (%)	
		Pirimiphos-methyl	R36341
Corn grain			
0	10	100.1 91.2	
	0.1		110.1 129.8
1	10	82.2 78.0	
	0.1		75.5 73.8
2	10	80.4 86.0	
	0.1		75.4 89.7
4	10	83.7 80.1	
	0.1		73.7 77.7
Sorghum grain			
0	10	91.2 96.7	
	0.1		109.4 77.1
1	10	64.7 63.9	
	0.1		82.1 69.3
2	10	54.4 63.3	
	0.1		46.4 70.5
4	10	58.1 59.3	
	0.1		43.1 59.0

Pirimiphos-methyl and R36341 residues in corn grain showed an average initial decline of 16% and 45%, respectively, in residue levels after 1 month of frozen storage; however, subsequent analyses at 2 and 4 months showed no further decline in residues. A similar situation was observed for residues of pirimiphos-methyl in stored sorghum grain; residues declined by 30% after 1 month of frozen storage and were stable thereafter. A steady decline in residue levels was observed only for residues of R36341 in sorghum grain; residues declined steadily from 93% at time-zero to 51% by 4 months. Although there is an apparent decline in residues of pirimiphos-methyl and R36341 in grain during frozen storage, HED is unable to determine an appropriate decline factor to be applied to residues in treated samples.

Additional storage stability data were submitted (1996; MRID 44039501) reflecting grain and corn oil storage intervals of 1483-1560 days (4-4.3 years). Corn, sorghum, and wheat grain were treated in 1988 with pirimiphos-methyl at 1x the registered rate. Grain and corn oil were originally analyzed in 1988-1989 after unspecified harvest-to sampling intervals and placed in frozen storage until a re-analysis was performed in 1993. The results of these analyses are shown in Table 9. Pirimiphos-methyl residues declined by 45% in corn grain and were relatively stable in sorghum grain and refined corn oil. There was an apparent 47% increase in pirimiphos-methyl residues in wheat grain.

The submission did not report the storage intervals or conditions of the samples prior to the first analysis. Furthermore, given the wide variation in stability reported for the various dry stored grains over 4 years, HED cannot use these data to determine a decline factor to apply to residues in samples stored for 1-32 months prior to analysis. Due to the variability in the results of the submitted storage stability data, the registrant should conduct a new storage stability study. Grain (corn or sorghum), corn oil, and aspirated grain fractions should be fortified with pirimiphos-methyl and R36341 at appropriate levels, stored frozen, and analyzed after intervals representative of the storage intervals incurred in the corn, sorghum, and wheat residue studies.

Table 9. Stability of Pirimiphos-Methyl in Grain and Corn Oil Stored Frozen for >4 Years.

Matrix	Original residue, 1988-1989 (ppm)	Storage interval (days)	Residue after storage, 1993 (ppm)	Percent change
Corn grain	4.9	1496	2.7	-45
Refined corn oil	11.8	1483	10.3	-13
Sorghum grain	6.0	1560	5.5	-8
Wheat grain	5.3	1487	7.8	+47

HED Comment

The available storage stability data are not adequate to support the submitted residue and processing studies for grain. However, the studies depicting the magnitude of pirimiphos-methyl residues in stored grain and processed commodities are adequate to support the registered use and tolerance reassessment, pending submission of acceptable storage stability data.

The submitted data indicate that tolerances for residues in sorghum and corn grain should be increased to 20 ppm. Based on the 20 ppm tolerance for residues in grain, the tolerance for residues in corn oil should be increased to 160 ppm. In addition, a tolerance for residues in aspirated grain fractions is required, at 50 ppm. Tolerances for residues in sorghum and corn milled fractions should be revoked [residues did not concentrate in corn milled fractions, and EPA no longer sets tolerances for residues in sorghum milled fractions]. If a tolerance is established for pirimiphos-methyl residues in wheat grain, a separate tolerance for residues in wheat flour will not be required.

HED notes that the reassessment of grain tolerances at higher levels may result in unacceptable dietary risks; if acceptable storage stability data demonstrate significant declines in residue levels during the storage intervals incurred in the submitted studies, then tolerances may need to be reassessed even higher. The submitted residue data could support lower tolerances, if fewer applications are specified. An immunoassay method for determining residues in stored grain has been validated by the Agency. SRRD may want to consider consulting with OGC to determine the feasibility of various approaches for risk managment.

MASTER RECORD IDENTIFICATION NUMBERS

44039501 Roper, E. (1993) Actellic: Stability of Residues of Pirimiphos-Methyl in Frozen Samples of Corn, Wheat and Sorghum Grain and in Refined Corn Oil: Lab Project Number: PIRI-93-SS-01: RR 93-030B. Unpublished study prepared by Zeneca Ag Products. 24 p.

44073901 Kliskey, E. (1996) Determination of the Magnitude of Residues of Pirimiphos-methyl in Stored Sorghum Grain Treated with Actellic 5E: Lab Project Number: WECO-9309: WECO-9309-CA1: WECO-9309-GA1. Unpublished study prepared by Compliance Services International. 343 p.

44073902 Kliskey, E. (1996) Determination of the Magnitude of Residues of Pirimiphos-methyl in Stored Corn Grain Treated with Actellic 5E: Lab Project Number: RR 5E: Lab Project Number: WECO-9310-CA1: WECO-9310-GA1: WECO-9310. Unpublished study prepared by Compliance Services International. 344 p.

44097801 Kliskey, E. (1996) Determination of the Magnitude of Residues of Pirimiphos-methyl in Processed Fractions of Stored Sorghum Grain Treated with Actellic 5E:

Lab Project Number: WECO-9316: WECO-9309: WECO-9316-TX1. Unpublished study prepared by Compliance Services International. 206 p.

44129601 Kliskey, E. (1996) Determination of the Magnitude of Residues of Pirimiphos-methyl in Processed Fractions of Wheat Treated with Actellic 5E: Lab Project Number: WECO-9208: WECO-9208-P: CSI-011. Unpublished study prepared by Compliance Services International. 232 p.

44155701 Kliskey, E. (1996) Determination of the Magnitude of Residues of Pirimiphos-methyl in Processed Fractions of Stored Corn Grain Treated with Actellic 5E: Lab Project Number: WECO-9315: WECO-9315-TX1: WECO-9310. Unpublished study prepared by Compliance Services International. 247 p.